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Hollow metallic microspheres produced by spark erosion

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Hollow spherical particles of Ni, CoFe, the ferromagnetic shape memory alloy $\text{Ni}_{49}\text{Mn}_{30}\text{Ga}_{21}$, and the giant magnetostrictive alloy $\text{Fe}_{83}\text{Ga}_{17}$, with diameters up to several tens of microns were produced by spark erosion, using liquid nitrogen as the dielectric liquid. In contrast, the particles were primarily solid when the dielectric liquid was argon. The wall thicknesses of the hollow particles depended on the elemental composition. Different models are considered to account for the formation of the spark-eroded hollow spheres, and some of the potential benefits to be derived from their use are described. © 2004 American Institute of Physics. [DOI: 10.1063/1.1779962]

In this letter we discuss a method for producing hollow spheres and microspheres (HSMs). All these HSMs are ferromagnetic, and some have specific applications, such as giant magnetostriction, ferromagnetic-shape-memory properties, and power devices. HSMs composed of inorganic and organic materials have numerous and diverse applications. Methods used for the synthesis of hollow spheres include:¹

- (1) Sacrificial cores—Spherical cores are coated with the material of interest, and the cores are subsequently dissolved or volatilized.
- (2) Nozzle-reactor systems—Specially designed atomizer nozzles dispense droplets of materials which are subsequently formed into hollow spheres in a reactor.
- (3) Emulsion/phase separation techniques—A wide range of these techniques have been developed, specifically tailored to the application/material objective.

Almost all reported HSMs are composed of organic or ceramic materials, but some examples of metallic HSMs have been described. Significant porosity or hollow structure has been reported in particles of 304L stainless steel, Cu, and the Ni-based superalloy RENÉ 95, which were atomized with argon or nitrogen.² A variation of the sacrificial core method, involving the mixing of metallic powders and styrofoam spheres in a fluid bed with subsequent sintering, has been used to prepare uniform metallic HSMs with diameters in the mm range.³ One method using a pulsed microarc discharge initiated between a consumable wire anode and a tool cathode, produced uniform droplets of 50–1000 μm diameter, which were hollow in the cases of W or Mo.⁴ Electroless deposition of $\sim 2 \mu\text{m}$ Co–Fe films on hollow ceramic spheres with an average diameter of $\sim 70 \mu\text{m}$ was reported.⁵

We have prepared metallic HSMs of different chemical compositions using spark erosion. The outside diameters of these HSMs range up to several tens of μm , and the shell thicknesses vary with composition. Details of the spark erosion method are discussed in Refs. 6 and 7. For this letter, it is sufficient to note that the process essentially consists of generating pulsed sparks between pieces of the material of interest, which are immersed in a dielectric liquid. The spark produces superheated localized regions (where it occurs). When the spark collapses, molten particles are ejected from these boiling regions, and then quenched *in situ* in the dielectric liquid or its vapor. Particles of virtually any material can be produced by spark erosion in sizes from a few tens of nm to 50 μm or more.

Particles of Ni, $\text{Co}_{50}\text{Fe}_{50}$, the ferromagnetic-shape-memory alloy $\text{Ni}_{49}\text{Mn}_{30}\text{Ga}_{21}$, and the giant magnetostrictive alloy $\text{Fe}_{83}\text{Ga}_{17}$ were prepared by spark erosion in the shaker-pot apparatus,⁷ using a relaxation oscillator which provided power pulses of $\sim 0.5 \text{ J}$ at a rate of $\sim 100 \text{ Hz}$. The dielectric liquids used were liquid nitrogen and argon. Spark erosion with these cryogenic liquids was carried out in a vacuum-sealed shaker-pot, and powder handling was done in an argon environment ($\sim 1 \text{ ppm}$ impurity) in a glove box. The starting electrodes and charge pieces⁷ of the four metal/alloy systems were provided by ACI Alloys.⁸ Particles were mounted in epoxy and mechanically polished to reveal their cross-sectional structure using scanning electron microscopy (SEM).

The powders prepared in liquid nitrogen or argon maintained the same composition as the starting electrodes and charge materials, as determined by x-ray, chemical, and energy dispersive spectroscopy analyses. The porosity of the particles prepared in liquid nitrogen was evident by visual inspection, since they clearly had a much lower density than those prepared in liquid argon. Figure 1 shows SEM micrographs of polished samples of Ni, $\text{Co}_{50}\text{Fe}_{50}$, $\text{Ni}_{49}\text{Mn}_{30}\text{Ga}_{21}$,

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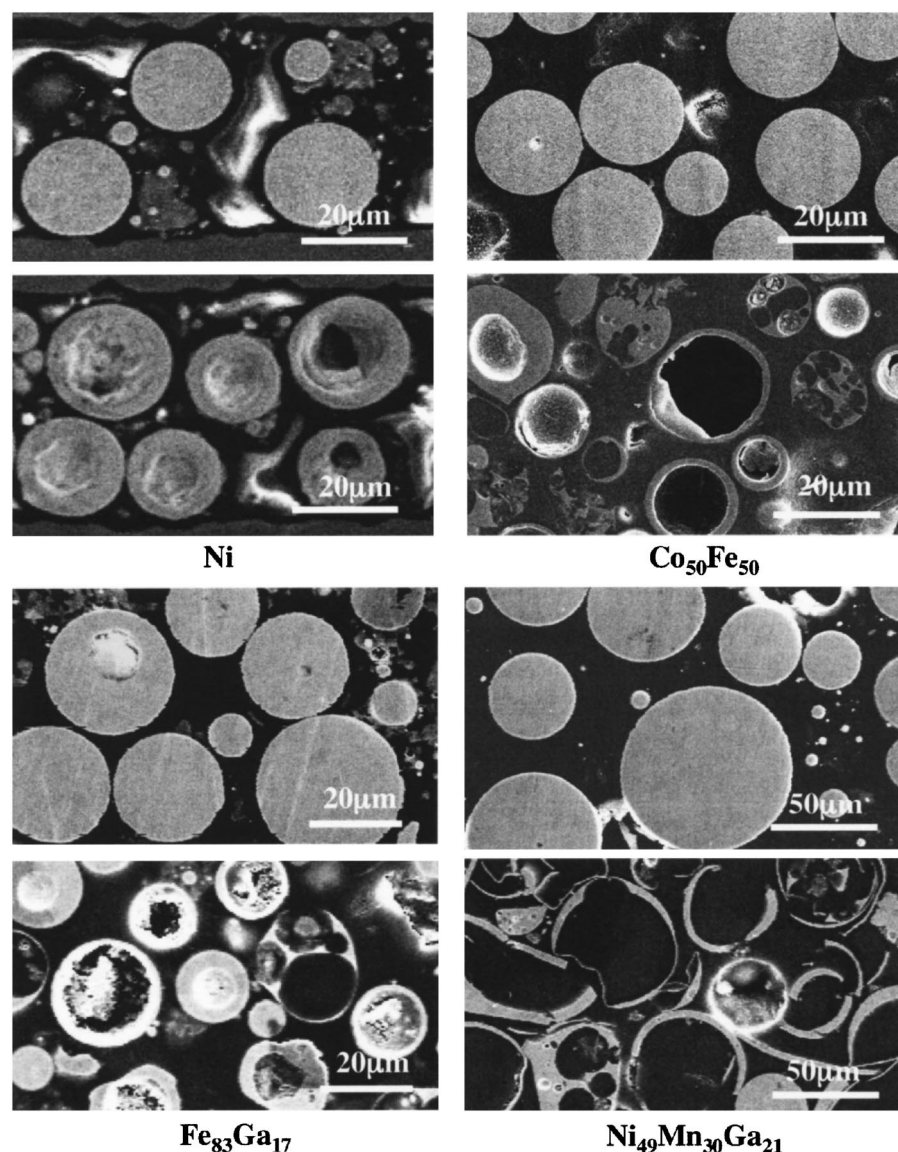


FIG. 1. SEM micrographs of mechanically polished cross sections of as-prepared particles of Ni, $\text{Co}_{50}\text{Fe}_{50}$, $\text{Fe}_{83}\text{Ga}_{17}$, and $\text{Ni}_{49}\text{Mn}_{30}\text{Ga}_{21}$ spark eroded in liquid argon (upper) and liquid nitrogen (lower).

and $\text{Fe}_{83}\text{Ga}_{17}$ powders as prepared in liquid argon and nitrogen. All particles prepared in liquid argon exhibit negligible porosity, whereas the powders prepared in liquid nitrogen are primarily hollow. Furthermore, it was determined from transmission electron micrographs of the $\text{Ni}_{49}\text{Mn}_{30}\text{Ga}_{21}$ particles that those produced in liquid argon were composed mainly of very large crystalline grains, whereas the particles prepared in liquid nitrogen were composed mainly of very small crystallites. This result suggests that particles sparked in argon cool more slowly than those prepared in liquid nitrogen. Such a difference in cooling rates is consistent with the fact that nitrogen has a thermal conductivity 44% greater than argon and a constant volume heat capacity 5.5 times that of argon. Thus, the molten sparked particles in argon would be enclosed in thicker vapor shells than for nitrogen, with slower heat extraction than for nitrogen. The shells of the hollow Ni and $\text{Fe}_{83}\text{Ga}_{17}$ particles are generally thicker than for the hollow $\text{Co}_{50}\text{Fe}_{50}$ and $\text{Ni}_{49}\text{Mn}_{30}\text{Ga}_{21}$. All hollow particles have some degree of internal structure, either in the form of large central pores ($\text{Co}_{50}\text{Fe}_{50}$ and $\text{Ni}_{49}\text{Mn}_{30}\text{Ga}_{21}$), or enclosed smaller particles ($\text{Fe}_{83}\text{Ga}_{17}$). It appears that the more nonspherical particles tend to possess large multiple pores. The Ni hollow particles show rough internal surfaces.

Reference 2 describes three mechanisms for hollow particle formation that are relevant for the spark-eroded particles described here.

- (i) **Bagging:** A molten platelet can close on itself to form a bubble that may contain vaporized cryogen, or even smaller particles.
- (ii) **Density gradient:** A molten droplet solidifies initially on its surface. Thus, complete solidification will leave a small central pore, since the density of the molten core is less than that of the solid.
- (iii) **Cryogen solubility:** Vaporized cryogen may be soluble at high temperatures in a molten droplet, but insoluble, or much less soluble, at lower temperatures after complete solidification. This leads to trapped gas within the particle.

By considering Fig. 1 in terms of these mechanisms, some possible origins of the observed structures may be inferred (without a high degree of confidence). The very low pore density of all particles prepared in argon, and the tiny sizes of those pores, is consistent with the *density gradient* mechanism. The high porosity of the particles prepared in liquid nitrogen is inconsistent with the *density gradient*

mechanism. *Bagging* is a likely mechanism for the $\text{Fe}_{83}\text{Ga}_{17}$ particles produced in liquid nitrogen, inasmuch as some have enclosed smaller particles. The thin shells of the more spherical $\text{Co}_{50}\text{Fe}_{50}$ and $\text{Ni}_{49}\text{Mn}_{30}\text{Ga}_{21}$ particles prepared in liquid nitrogen suggest an initial platelet formation, consistent with *bagging*, although there is no significant evidence for enclosed smaller particles. However, the irregularly shaped particles in both systems have large multiple pores, which suggests that *cryogen solubility* may also be involved. When the as-sparked $\text{Ni}_{49}\text{Mn}_{30}\text{Ga}_{21}$ particles prepared in nitrogen were annealed in a vacuum to stabilize the martensite phase, a large temporary increase in pressure was always noted at $\sim 300^\circ\text{C}$. This behavior may indicate the bursting of some hollow spheres and the liberation of enclosed nitrogen. Both *bagging* and *cryogen solubility* would produce this result. The Ni particles prepared in nitrogen have thicker shells and rougher internal structures than the other similarly prepared ones. These hollow Ni particles also show porosity in their shells. Both properties may indicate *cryogen solubility*.

The advantages of HSMs are exemplified by $\text{Ni}_{49}\text{Mn}_{30}\text{Ga}_{21}$, a ferromagnetic-shape-memory alloy in which strains as large as 6%, due to twin boundary motion, can be induced by applying magnetic fields.⁹ This makes $\text{Ni}_{49}\text{Mn}_{30}\text{Ga}_{21}$ a promising candidate for actuator or energy-absorber applications. However, this alloy is very brittle, and cannot support significant stress in bulk form. A solution to this problem was provided by preparing composites consisting of $\text{Ni}_{49}\text{Mn}_{30}\text{Ga}_{21}$ particles that were spark-eroded in liquid nitrogen¹⁰ disposed in a polymer matrix. These composites exhibited the desired stress-induced twin-boundary motion with significant hysteresis.¹¹ The fact that the $\text{Ni}_{49}\text{Mn}_{30}\text{Ga}_{21}$ particles were hollow provides an additional advantage, in that the weight of these composites is much less than composites made with an equivalent volume fraction of solid $\text{Ni}_{49}\text{Mn}_{30}\text{Ga}_{21}$ particles. $\text{Fe}_{83}\text{Ga}_{17}$ exhibits magnetostrictive strains of several hundred ppm,^{12,13} which

makes it attractive for the same applications as $\text{Ni}_{49}\text{Mn}_{30}\text{Ga}_{21}$. Again, hollow particles in these composites offer a significant weight reduction. Another potential advantage in using hollow polycrystalline particles is that they may suffer less reduction in field-induced strain arising from confinement by neighboring crystallites than solid particles or bulk samples of $\text{Ni}_{49}\text{Mn}_{30}\text{Ga}_{21}$ or $\text{Fe}_{83}\text{Ga}_{17}$. Finally, CoFe hollow particles are useful for high-frequency applications, such as microwave absorption⁵ and power transmission devices.

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